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DESCRIPTION

ELECTRODEPOSITED COPPER FOIL WITH LOW ROUGHNESS SURFACE AND PROCESS FOR PRODUCING THE SAME

TECHNICAL FIELD

The present invention relates to electrodeposited copper foil with low roughness surface and processes for producing the same, the copper foils having roughness surface uniformly provided with low roughness without uneven surge and being applicable in printed-wiring boards or cathode collectors of lithium secondary battery.

BACKGROUND ART

One conventional process for producing an electrodeposited copper foil well known in the art includes passing a direct current between an insoluble anode consisting of a titanium plate coated with a Platinum Group element or oxide thereof and a titanium drum as a cathode counter to the anode in an electrolyte of an aqueous solution of sulfuric acid/copper sulfate to allow electrodeposited copper to precipitate on the surface of the titanium drum, while peeling off the precipitated electrodeposited copper from the surface of the titanium drum rotating at a constant speed and continuously winding up the same.

In the present description, the face of electrodeposited copper foil that has contacted the drum surface is referred to as “gloss surface” and the face opposite to the gloss surface is referred to as “roughness surface”.

Electrodeposited copper foil produced in the manner as described above are called "copper foil without treatment" by those skilled in the art, and are not usually used in the form of copper foil without treatment. For use as electrodeposited copper foil for printing circuit, they will undergo a roughness providing process for improving the adhesivity relative to a resin and various surface treatment processes for imparting thermal resistance, chemical resistance and antirust ability before provided as products.

In traditional approach, mountain and valley shapes in the roughness surface are sharpened (made rough) by adding 10 to 100 mg/L of chloride ions and 0.1 to 4.0 mg/L of glue or gelatin into the electrolyte used in production of electrodeposited copper foil, without treatment, however, in recent application of electrodeposited copper foil such as for a printed-wiring board or for a cathode collector for lithium secondary battery, an electrodeposited copper foil whose surface roughness on its roughness surface is as small as possible and having a least difference in surface roughness between roughness surface and gloss surface (since the gloss surface copies a flat shape of the cathode drum surface, there essentially arises a difference in roughness between the gloss surface and the roughness surface) and having a small thickness is requested.

This arises from the request from the view point of improvement in circuit accuracy associated with increased fineness of lines or patterns in the case of printed-wiring board, and arises from the fact that a difference in roughness between gloss surface and roughness surface, namely a difference in battery reaction based on a difference in surface area is no longer necessary to be considered in the case of cathode collector for lithium

secondary battery.

However, it is difficult to reduce the difference in roughness between gloss surface and roughness surface, while satisfying various practicable mechanical characteristics.

It is within the conventional knowledge that in a process for producing an electrodeposited copper foil, by appropriately selecting and adding to an electrolyte various kinds of water-soluble polymer substances, various kinds of surfactants, various kinds of organosulfur compounds, chloride ions and the like, the difference in roughness between gloss surface and roughness surface can be made as small as possible. As such a technique, Japanese Published Patent Publication No. 2002-506484, for example, discloses that an electrodeposited copper foil (electrodeposited copper foil, without treatment) having a fine projecting end of about 3.8 μm or less in height on its roughness surface is obtained when low-molecular-weight water-soluble cellulose ether, low-molecular-weight water-soluble polyalkyleneglycol ether, low-molecular-weight water-soluble polyethyleneimine and water-soluble sulfonated organosulfur compound are added to an electrolyte. Japanese Patent Publication No. 3313277, for example, discloses that an electrodeposited copper foil (electrodeposited copper foil, without treatment) realizing low roughness of roughness surface and small difference in roughness between gloss surface and roughness surface and exhibiting excellent elongation at high temperature is obtained when cellulose ether, low-molecular-weight glue, a compound having a mercapto group and chloride ions are added to an electrolyte.

The present inventors carried out many experiments for obtaining an

electrodeposited copper foil while appropriately combining and adding, to an electrolyte composed of an aqueous solution of sulfuric acid/copper sulfate various water-soluble polymer substances, various organosulfur compounds, chloride ions and the like disclosed in the aforementioned publications. The resultant electrodeposited copper foil had low roughness on the roughness surface of the electrodeposited copper foil, however, moderate uneven surge still occurred on the roughness surface (see Fig. 7 below).

The moderate uneven surge occurring on the roughness surface of the electrodeposited copper foil (electrodeposited copper foil, without treatment) may induce abnormal precipitation of copper crystalline particles during the aforementioned step of providing roughness, and increase surface roughness (Rz) of a roughness surface of product.

In application of flexible printed-wiring board, a copper foil undergoes heat history in the step of adhesion with an insulating film, and when copper crystalline particles are small in size, they will grow and become bulky through this heat history.

In view of the above, the technical issue of the present invention is to provide an electrodeposited copper foil with low roughness surface having roughness surface uniformly provided with low roughness without uneven surge and being applicable in printed-wiring boards or cathode collectors of lithium secondary battery, more particularly to provide an electrodeposited copper foil with low roughness surface wherein surface roughness (Rz) is 2.0 μm or less, surface uniformity is provided with low roughness without uneven surge and a percent elongation is 10.0% or higher at 180°C.

The present inventors made diligent researches for dealing with the

above technical issue, and found that an electrodeposited copper foil with low roughness surface having surface roughness (Rz) of 2.0 μm or less, surface uniformity provided with low roughness without uneven surge and exhibiting a percent elongation of 10.0% or higher at 180°C can be obtained when four additives, polyoxyethylene surfactant, polyethyleneimine or its derivative, sulfonate of active organosulfur compound and chloride ions are contained in an electrolyte of an aqueous solution of sulfuric acid/copper sulfate, and finally accomplished the above issue.

DISCLOSURE OF THE INVENTION

That is, the present invention is directed to an electrodeposited copper foil with low roughness surface, wherein surface roughness (Rz) is 2.0 μm or less, surface uniformity is provided with low roughness without uneven surge, and a percent elongation is 10.0% or higher at 180°C.

The present invention is also directed to the electrodeposited copper foil with low roughness surface, wherein degree of mirror gloss of the roughness surface, measured by Gs (85°) in accordance with JIS (Japanese Industrial Standard) Z 8741 is 100 or more.

The present invention is also directed to a process for producing an electrodeposited copper foil with low roughness surface having surface roughness (Rz) of 2.0 μm or less, surface uniformity provided with low roughness without uneven surge and exhibiting a percent elongation of 10.0% or higher at 180°C, comprising passing a direct current between an insoluble anode consisting of a titanium plate coated with a Platinum Group element or oxide thereof and a titanium drum as a cathode counter to the

anode in an electrolyte of an aqueous solution of sulfuric acid/copper sulfate, wherein the electrolyte contains an oxyethylene surfactant, a polyethyleneimine or its derivative, a sulfonate of active organosulfur compound and chloride ions.

The present invention is also directed to the process for producing an electrodeposited copper foil with low roughness surface, wherein degree of mirror gloss of the roughness surface, measured by Gs (85°) in accordance with JIS Z 8741 is 100 or more in the electrodeposited copper foil with low roughness surface.

The present invention is also directed to the process for producing an electrodeposited copper foil with low roughness surface, wherein concentration of oxyethylene surfactant in the electrolyte is in the range of 10 to 200 mg/L.

The present invention is also directed to the process for producing an electrodeposited copper foil with low roughness surface, wherein concentration of polyethyleneimine or its derivative in the electrolyte is in the range of 0.5 to 30.0 mg/L.

The present invention is also directed to the process for producing an electrodeposited copper foil with low roughness surface, wherein concentration of sulfonate of active organosulfur compound in the electrolyte is in the range of 5.5 to 450 μmol/L.

The present invention is also directed to the process for producing an electrodeposited copper foil with low roughness surface, wherein concentration of chloride ions in the electrolyte is in the range of 20 to 120 mg/L.

In the following, the present invention will be explained in more detail.

In the present invention, the additives added to the electrolyte of an aqueous solution of sulfuric acid/copper sulfate are oxyethylene surfactant, polyethyleneimine or its derivative, sulfonate of active organosulfur compound and chloride ions, and an intended electrodeposited copper foil with low roughness surface can be obtained only when these additives are present at certain ranges of concentration, and soluble polymers are within certain ranges of molecular weight.

Examples of the oxyethylene surfactant used in the present invention include polyethylene glycol having an average molecular weight of 2000 to 35000; polyoxyethylene-polyoxypropylene copolymer in which an average molecular weight of oxypropylene is in the range of 2000 to 4000 and a ratio by weight of oxyethylene in the total molecular weight is 80 wt% or more; polyoxyethylene lauryl ether; polyoxyethylene nonylphenyl ether; bisphenol A-ethyleneoxide adduct and the like. Here, those having a ratio by weight of oxyethylene in the total molecular weight is 80 wt% or less are insoluble in the electrolyte of an aqueous solution of sulfuric acid/copper sulfate.

When the average molecular weight of polyethylene glycol is 2000 or less, abnormal electric deposition will occur on the surface of the electrodeposited copper foil.

In the present invention, one or combination of two or more of the above compounds is added into the electrolyte so that the concentration of the one or the combination in the electrolyte is in the range of 10 to 200 mg/L.

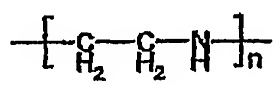
The lower limit of this concentration range is important and represents a threshold up to which an intended electrodeposited copper foil with low roughness surface is not obtained even if concentrations of the polyethyleneimine and its derivative, the sulfonate of active organosulfur compound and the chloride ions are adjusted to the respective optimum concentration ranges as recited below. On the other hand, the upper limit does not represent a threshold that determines whether an intended electrodeposited copper foil with low roughness surface is obtained or not as is the case of the lower limit, and keeping the concentration at high values in an industrial operative condition gives no positive meaning from the view point of economics. Therefore, the upper limit defined above is not intended to define characteristics of an obtainable electrodeposited copper foil. An intended electrodeposited copper foil with low roughness surface may also be actually obtained using the range exceeding the above upper limit, however such measure is not practical.

A lower limit of average molecular weight is also important, and at an average molecular weight of less than 2000, an intended electrodeposited copper foil with low roughness surface is not obtained. As to the upper limit, as is the same with the upper limit of the concentration range, an intended electrodeposited copper foil with low roughness surface is very likely to be obtained even when polyethylene glycol having an average molecular weight of greater than 35000 is used.

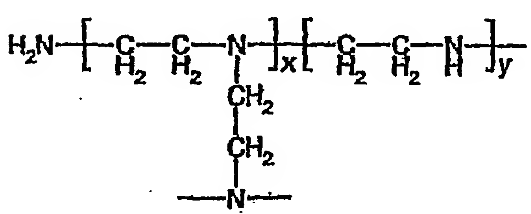
Uneven moderate surge is still observed on the roughness surface of an electrodeposited copper foil obtainable by adding oxyethylene surfactant, active organosulfur compound and chloride ions into an electrolyte, however,

occurrence of such surge may be controlled by adding polyethyleneimine.

Polyethyleneimine used in the present invention has a weight average molecular weight of desirably 600 or more, and more desirably 10000 or more. It may be of the straight form shown in the following chemical formula (1) or the branched form shown in the following chemical formula (2) or of mixture of both insofar as it has a weight average molecular weight of 600 or more.



(Chemical Formula 1)



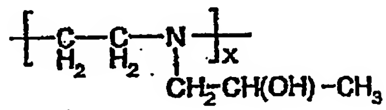
(Chemical Formula 2)

One exemplary commercial product is "EPOMIN (product name), Product number: P-1000, Nippon Shokubai Co., Ltd., weight average molecular weight: 70000".

As the derivative of polyethyleneimine, propylene oxide adducts having a weight average molecular weight of 1000 or more are desirable, and polyethyleneimine to which propylene oxide is added desirably has a molecular weight of 600 or more.

As shown in the following chemical formula (3), it is desirable that substituents to a tertiary amine hydrogen and a secondary amine hydrogen

of polyethyleneimine are provided.



(Chemical Formula 3)

One exemplary commercial product is “EPOMIN (product name), Product number: PP-061, Nippon Shokubai Co., Ltd., weight average molecular weight: 1200”.

When the polyethyleneimine has a weight average molecular weight of less than 600, and the derivative of polyethyleneimine has a weight average molecular weight of less than 1000, the resultant electrodeposited copper foil has moderate uneven surge on its roughness surface and glossy appearance is not realized (uniform low roughness is not obtained) regardless of concentrations thereof. When moderate uneven surge does not occur on the roughness surface and hence uniform low roughness is provided, the appearance is glossy. On the other hand, when moderate uneven surge occurs on the roughness surface and hence uniform low roughness is not provided, the appearance is semi-glossy or drab.

As a general tendency of relationship between concentration region and molecular weight of polyethyleneimine and its derivative, the larger the molecular weight, the higher the concentration threshold at which the roughness surface begins to change from semi-glossy to glossy, and the concentration at which it begins to change to “burnt deposits” region where powder copper precipitates rather than formation of a plating film also shifts

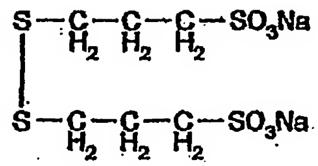
to higher concentration. Even within the glossy region, percent elongation at high temperature decreases with increase in concentration of polyethyleneimine. It is necessary to determine the ranges of molecular weight and concentration in consideration of the effects of molecular weight and concentration exerted by such polyethyleneimine and its derivative, and polyethyleneimine and its derivative desirably has a molecular weight of 600 to 70000, and the concentration thereof in an electrolyte is desirably in the range of 0.5 to 30.0 mg/L, and preferably in the range of 1.0 to 10.0 mg/L.

When the concentration of the polyethyleneimine and its derivative in the electrolyte is less than 0.5 mg/L, the roughness surface exhibits drab appearance, and when it exceeds 30 mg/L, an electrodeposited copper foil is no longer obtained because "burnt deposits" region is reached.

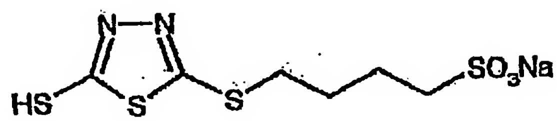
It is essential that an active organosulfur compound used in the present invention is a compound obtained by solubilizing slightly soluble in water alkylthiol. However, when a hydroxyl group or a carboxyl group is added for solubilization, it is impossible to obtain an intended electrodeposited copper foil with low roughness surface. Therefore, it is necessary to achieve solubilization in the form of sulfonate salt. Representative sulfonate salts of active organosulfur compound suited for the present invention are shown in the following chemical formulas (4), (5), (6) and (7).

$$HS-\underset{H_2}{C}-\underset{H_2}{C}-\underset{H_2}{C}-SO_3Na$$

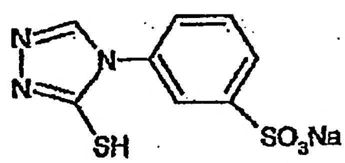
(Chemical Formula 4)



(Chemical Formula 5)



(Chemical Formula 6)



(Chemical Formula 7)

It is unreasonable to express adding amounts of these compounds in concentration by mass. Considering the fact that effects of these compound are determined by thiol group existing in their structures, the compound shown by the chemical formula (5) which is a dimmer of 3-mercapto-1-propane sulfonic acid shown by the chemical formula (4) generates two thiol groups, and hence a single molecule exerts double effect compared to sodium 3-mercapto-1-propane sulfonate. For this reason, an adding amount may be defined by molar number of thiol groups existing in a molecule.

Expressing the existing amount of thiol group by molar concentration, a preferred adding amount (molar concentration) to electrolyte of the active organosulfur compound in the present invention is desirably in the range of 5.5 to 450 μmol/L, preferably in the range of 55 to 180 μmol/L. When the

concentration in an electrolyte is less than 5.5 μmol/L, the roughness surface has moderate uneven surge, lacks low roughness, and exhibits drub appearance and no gloss. Also percent elongation at 180°C is poor. Although no effects are exerted on the condition of roughness surface and percent elongation at 180°C even when the adding amount exceeds 450 μmol/L, keeping high concentration of active organosulfur compound in an electrolyte is not practical, because expensive organosulfur compound is wastefully decomposed and consumed due to high anode potential in production of an electrodeposited copper foil using an insoluble anode.

In the present invention, presence of chloride ions is very important, and an intended electrodeposited copper foil with low roughness surface is not obtained only by adjusting the oxyethylene surfactant, the polyethyleneimine or its derivative and the sulfonate of active organosulfur compound to the respective concentration ranges. The object of the present invention is achieved only when chloride ions are present.

Also important is a concentration relationship between chloride ion and active organosulfur compound which are determinants for a concentration range in which glossy appearance of roughness surface (roughness surface is provided with uniform roughness without uneven moderate surge on the roughness surface) is exhibited. This gloss range tends to diminish as the chloride ion concentration increases, and in order to operate with lower concentration of active organosulfur compound, it is desirable to use lower concentration of chloride ions. Accordingly, concentration of chloride ions in an electrolyte is desirably in the range of 20 to 120 mg/L, and preferably in the range of 30 to 100 mg/L. When the

concentration of chloride ions is less than 20 mg/L, the roughness surface will not be roughened to as low as 2.0 μm or less. When chloride ions exceeding 120 mg/L are used, rough deposits will occur on a plated surface.

A source of chloride ions may be inorganic salts that dissociate in an aqueous solution and release chloride ions, and typical examples include NaCl, HCl and the like.

In the present invention, it is possible to obtain an intended electrodeposited copper foil with low roughness surface by electrolysis under an electrolyte temperature of 35 to 50°C and an electrolytic current density of 30 to 50A/dm^2, using an electrolyte of an aqueous solution of sulfuric acid/copper sulfate in which the four additives, oxyethylene surfactant, polyethyleneimine or its derivative, sulfonate of active organic ion compound and chloride ions are adjusted to the respective optimum concentration ranges, and using an anode consisting of a titanium plate coated with a Platinum Group element and a cathode consisting of a titanium drum.

BRIEF DESCRIPTION OF THE DRAWINGS

Fig. 1 is an electromicrogram (x1000 magnification) of a roughness surface of an electrodeposited copper foil (electrodeposited copper foil, without treatment) obtained in the best mode for carrying out the present invention.

Fig. 2 is an electromicrogram (x1000 magnification) of a roughness surface of an electrodeposited copper foil (electrodeposited copper foil, without treatment) obtained in Comparative Example 1.

Fig. 3 is an electromicrogram (x1000 magnification) of a roughness

surface of an electrodeposited copper foil (electrodeposited copper foil, without treatment) obtained in Comparative Example 3.

Fig. 4 is an electromicrogram (x1000 magnification) of a roughness surface of an electrodeposited copper foil (electrodeposited copper foil, without treatment) obtained in Comparative Example 4.

Fig. 5 is an electromicrogram (x1000 magnification) of a roughness surface of an electrodeposited copper foil (electrodeposited copper foil, without treatment) obtained in Comparative Example 6.

Fig. 6 is an electromicrogram (x1000 magnification) of a roughness surface of an electrodeposited copper foil (electrodeposited copper foil, without treatment) obtained in Comparative Example 7.

Fig. 7 is an electromicrogram (x1000 magnification) of a roughness surface of an electrodeposited copper foil (electrodeposited copper foil, without treatment) obtained by using an electrolyte to which polyethyleneimine is not added.

BEST MODE FOR CARRYING OUT THE INVENTION

Best mode for carrying out the invention will be described below.

An electrolyte of an aqueous solution of sulfuric acid/copper sulfate comprising 100 g/L of sulfuric acid (H_2SO_4) and 280 g/L of copper sulfate pentahydrate ($CuSO_4 \cdot 5H_2O$) was prepared (hereinafter, this electrolyte is referred to as "basic electrolyte").

As additives, polyethylene glycol (average molecular weight 20000, product of Sanyo Chemical Industries, Ltd.), polyethyleneimine ("EPOMIN (product name), Product number: P-1000, Nippon Shokubai Co., Ltd., weight

average molecular weight: 70000), sodium 3-mercapto-1-propane sulfonate, and hydrochloric acid were added to the basic electrolyte such that 30 mg/L of polyethylene glycol, 0.5 mg/L of polyethyleneimine, 220 μmol/L of sodium 3-mercapto-1-propanesulfonate and 35 mol/L of chloride ions were achieved.

The electrolyte containing these additives was allowed to flow between a titanium plate coated with an oxide of Platinum Group serving as an anode and a titanium drum serving as a cathode, and electrocrystallization was conducted at an electrolytic current density of 45 A/dm^2 and an electrolyte temperature of 40°C, to obtain an electrodeposited copper foil with low roughness surface having a thickness of 18 μm. Visual inspection revealed that a roughness surface of the electrodeposited copper foil with low roughness surface has gloss.

The electrodeposited copper foil with low roughness surface (electrodeposited copper foil, without treatment) thus obtained was measured for expansive force (MPa) and percent elongation (%) at room temperature (about 25°C) and at 180°C in accordance with IPC-TM-650 using Type 2001 tension tester available from INTESCO Co., Ltd., and measured for surface roughness (Rz) of roughness surface in accordance with JIS B 0601 using SURFCORDER SE 1700α available from Kosaka Laboratory Ltd. As an index for indicating degree of uneven surge on the roughness surface of the electrodeposited copper foil with low roughness surface, mirror gloss of the roughness surface was measured in two directions along width and length (flow) of the electrodeposited copper foil with low roughness surface in accordance with JIS Z 8741, using a gloss meter available from Minolta Co., Ltd. (product name: MULTIGLOSS TYPE

268) and by Gs (85°). Measurement results are shown in Table 1.

The degree of mirror gloss Gs (85°) will show values of 100 or more when uneven surge does not substantially occur on a roughness surface, while it will show values of less than 100 when moderate uneven surge occurs on a roughness surface (see Table 2 and Figs. 1 to 7 below). In other word, the degree of mirror gloss Gs (85°) is index of degree of uneven surge on a roughness surface, and the smaller the value, the larger the degree of uneven surge, and the larger the value, the smaller the degree of uneven surge.

Fig. 1 is an electromicrogram (x1000 magnification) of a roughness surface of an electrodeposited copper foil (electrodeposited copper foil, without treatment) obtained herein, demonstrating that the roughness surface has a roughness surface condition having uniform low roughness and substantially lacking uneven surge on the roughness surface.

Examples 1 to 7 of the present invention and Comparative Examples 1 to 9 are as follows.

An electrodeposited copper foil having a thickness of 18 μm was obtained in the same conditions as employed in the above best mode for carrying out the invention except that kinds and concentrations in electrolyte of additives and electrolytic current density and electrolytic liquid temperature were changed as shown in Table 1. Each electrodeposited copper foil (electrodeposited copper foil, without treatment) thus obtained was measured for expansive force (MPa) and percent elongation (%) at room temperature (about 25°C) and at 180°C, surface roughness (Rz) (μm), and degree of mirror glosses Gs (85°) in the width and length (flow) directions

according to the same measurement techniques as employed for measurements in the best mode for carrying out the invention. The results are shown in Table 2.

Table 1:

	Concentration of additive				Electrolytic condition	
	Polyethylene glycol (M.W. 20,000) (mg/L)	Polyethyleneimine (mg/L)	Sodium 3-mercapto-1-propanesulfonate (μmol/L)	Chloride ion concentration (mg/L)	Current density (A/dm^2)	Liquid temperature (°C)
Best mode for carrying out the invention	30	0.5[1]	220	35	45	40
Example 1	30	10.0[1]	220	35	45	40
Example 2	100	30.0[2]	140	35	50	45
Example 3	70[6]	1.0[1]	140	35	50	40
Example 4	200	1.0[2]	330	70	30	35
Example 5	10	6.0[2]	220	100	45	40
Example 6	25	10.0[2]	220	110	45	50
Example 7	20	20.0[2]	6.0	20	50	50
Comparative Example 1	70[3]	0.1[1]	140	35	45	40
Comparative Example 2	100	0.1[1]	140	35	45	40
Comparative Example 3	10	1.0[4]	170	35	45	40
Comparative Example 4	50	35.0[5]	170	35	45	40
Comparative Example 5	50	35.0[1]	140	35	45	40
Comparative Example 6	50	0.3[1]	140	35	45	40
Comparative Example 7	25	0.2[1]	3.0	35	45	40
Comparative Example 8	25	0.2[1]	140	150	45	40
Comparative Example 9	25	0.2[1]	140	2	45	40

(1) Average molecular weight: 70000, (2) Polyethyleneimine derivative (EPOMIN: product name, Product number: PP-061, Nippon Shokubai Co., Ltd.., weight average molecular weight: 1200), (3) Average molecular weight: 1000, (4) Average molecular weight: 300, (5) Average molecular weight: 600

Table 2

	Room temperature		180°C		Surface roughness (Rz)		Degree of mirror gloss of roughness surface Gs (85°)	
	Expansive force (MPa)	Percent elongation (%)	Expansive force (MPa)	Percent elongation (%)	Roughness surface (μm)	Gloss surface (μm)	Width direction	Length direction (flow direction)
Best mode for carrying out the invention	350	16.0	230	14.0	1.8	2.2	121	128
Example 1	390	12.0	250	10.0	1.7	2.2	120	125
Example 2	500	15.0	280	12.0	1.7	2.1	122	125
Example 3	350	10.0	220	20.0	2.0	2.1	130	128
Example 4	340	18.0	180	15.0	1.2	2.2	125	126
Example 5	350	12.0	210	14.0	1.5	2.1	120	118
Example 6	360	11.0	210	10.0	1.5	2.2	131	135
Example 7	360	15.0	205	20.0	0.9	2.2	132	136
Comparative Example 1	350	5.0	200	6.0	2.5	2.2	78	73
Comparative Example 2	350	6.0	200	3.0	4.5	2.2	60	62
Comparative Example 3	360	20.0	250	24.0	3.0	2.2	74	74
Comparative Example 4	480	5.5	365	3.0	3.0	2.2	38	41
Comparative Example 5	430	4.5	305	2.8	1.8	2.1	40	42
Comparative Example 6	335	10.0	230	14.0	2.8	2.1	63	63
Comparative Example 7	350	10.0	220	3.0	4.0	2.1	21	18
Comparative Example 8	360	7.0	230	7.0	3.0	2.2	20	22
Comparative Example 9	350	6.0	210	5.0	3.2	2.2	26	25

Figs. 2 to 6 are electromicrograms (x1000 magnification) of roughness surfaces of electrodeposited copper foil (electrodeposited copper foil, without treatment) obtained in the comparative examples. Fig. 2 shows a condition of roughness surface of Comparative Example 1 (average molecular weight of polyethylene glycol is low and concentration of polyethyleneimine is low), Fig. 3 shows a condition of roughness surface of Comparative Example 3 (weight average molecular weight of polyethyleneimine is low), Fig. 4 shows a condition of roughness surface of Comparative Example 4 (average molecular weight of polyethylene glycol is low and concentration of polyethyleneimine is high), Fig. 5 shows a condition of roughness surface of Comparative Example 6 (concentration of polyethyleneimine is low), and Fig. 6 shows a condition of roughness surface of Comparative Example 7 (concentration of sodium 3-mercapto-1-propanesulfonate is low).

Fig. 7 is an electromicrogram (x1000 magnification) of a roughness surface of an electrodeposited copper foil (electrodeposited copper foil, without treatment) having a thickness of 18 μm, obtained in the same condition with the best mode for carrying out the invention except that polyethyleneimine is not added, in which occurrence of moderate uneven surge on the roughness surface is observed. Comparison of Fig. 7 with Fig. 1 showing the best mode for carrying out the invention reveals that addition of polyethyleneimine significantly lowers the surface roughness without causing moderate uneven surge on the roughness surface.

Tables 1 and 2 show that in respective electrolytes according to the best mode for carrying out the invention and Example 1 to 7, the roughness

or roughness surface (Rz) is kept at almost a constant value, although the expansive force at room temperature increases with concentration of polyethyleneimine.

The present inventors also found from a number of experiments that when there is no polyethylene glycol in the basic electrolyte, the roughness surface does not exhibit glossy appearance; when there is no polyethyleneimine in the basic electrolyte, the roughness surface exhibits rough and drab appearance and has low percent elongation at 180°C; when there is no sodium 3-mercapto-1-propane sulfonate, the roughness surface is very rough and has low percent elongation at 180°C; and when there is no chloride ion, the electrodeposition surface (plated surface) cracks and the percent elongation at 180°C is low.

Also found is that when concentration or average molecular weight of water soluble polymer is increased within the above predetermine range, the degree of mirror gloss Gs (85°) tends to increase correspondingly. In order to obtain an electrodeposited copper foil with low roughness surface having a degree of mirror gloss Gs (85°) of 100 or more, it is preferred to contain polyethylene glycol, sodium 3-mercapto-1-propane sulfonate, polyethyleneimine and chloride ions in the basic electrolyte, however, lacking of either one of these substances or concentration or average molecular weight beyond the aforementioned predetermine ranges will render the degree of mirror gloss (85°) less than 100.

INDUSTRIAL APPLICABILITY

According to the present invention, it is possible to provide an

electrodeposited copper foil with low roughness surface (electrodeposited copper foil, without treatment) suitably applied to printed-wiring boards or cathode collectors of lithium secondary battery, having a roughness surface whose surface roughness Rz is 2.0 μm or less and degree of mirror gloss Gz (85°) is 100 or more with substantially no uneven surge on the roughness surface, the electrodeposited copper foil exhibiting a percent elongation of 10.0% or more at 180°C, and having a difference in surface roughness between gloss surface and roughness surface as small as possible.